THE MICROELEMENTS CONTENT IN THE ERODED CARBONATIC CHERNOZEM FROM CENTRAL AREA OF MOLDOVA

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Abstract

The chernozems carbonatic eroded on the territory of the Republic of Moldova occupy the area of 294 thousand ha (44.2% of the total area). These soils are most vulnerable to erosion processes in all chernozem subtypes. Loss of macro- and micro-nutrients on agricultural land is significant and has become an important issue for agricultural production. The results of Mn, Co, Zn, Cu, Ni determination (atomic absorption spectrophotometer) in the arable layer of eroded chernozem revealed that water erosion influences their distribution in soils. The average content in the non eroded carbonatic chernozem is: Mn - 654, Cu - 32, Co - 14, Zn - 38, Ni - 40 mg/kg. With increases of erosion degree, the total content of Cu, Zn, Co and Mn decreases in the range of 3-35%, the Ni content increases, from 6% to 78% compared to the non eroded soil. The losses of microelements in the heavily eroded carbonatic chernozem were: Cu - 35%, Zn - 31%, Mn - 27% compared to non eroded soil. The Mn, Zn, Co and Ni content in the eroded carbonatic chernozem is higher than the average quantity for carbonatic chernozems, and the Cu content is lower.

Key words: carbonatic chernozem, content, erosion, microelements

Chernozems carbonatic are widespread in the Republic of Moldova and occupy 654 thousand hectares in the steppe zone. These soils are distributed on the youngest floodplain terraces of the Dniester, Prut and small rivers, which are moving far to the north. Chernozems carbonatic are the youngest pedogeologically soils. According to the granulometric composition, they are mainly heavy loamy and loamy. The soils are characterized by the presence of carbonates from the surface layer, an alkaline reaction throughout the profile, an increased calcareous potential, a relatively insignificant humus content with a fairly large thickness of the humus horizon. These properties allow to distinguish them at the independent subtype level (Крупеников, 1979).

Chernozems carbonatic eroded on the territory of Moldova, occupy 294 thousand hectares or 44.2% of the total area. They are most vulnerable to erosion processes from all subtypes of chernozems. The loss of nutrient macro- and microelements on agricultural land is significant and has become an important problem for agricultural production.

Research has been carried out both to study the content of trace elements accessible to plants (in agrochemistry) and to determine the general biogeochemical content. Other chemical forms of soil microelements have not been studied or studied in partial. In this paper, we present the results of determining the total content and chemical forms of microelements (Mn, Cu, Zn, Co, Ni) in eroded carbonatic chernozems in dependence on the erosion degree.

MATERIAL AND METHOD

The research object were chernozems carbonatic of different erosion degrees, as well as diluvial layered carbonate soils. The study soils are located on the slope with length 1200 m, steepness of 8-10°. Eroded carbonate chernozems are a very peculiar group of soils, characterized by genetic features, many specific physical and chemical properties, agronomic and agrochemical characteristics. Unlike other subtypes, carbonate chernozems have an alkaline reaction in the vertical profile. Carbonates content of these soils reflects the conditions of nitrogen, phosphorous and trace elements mobility (Кабата - Пендиас & Пендиас, 1989; Атлас Почв Молдавии, 1988).

Determination of trace elements from soil samples was performed by atomic absorption spectrophotometer. The total content was determined by the classical method of decomposition with hydrofluoric acid in combination with sulfuric acid. Various conventional extracts were used to determine the chemical forms with the soil compounds (Содержание, 1979).

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RESULTS AND DISCUSSIONS

Carbonate chernozems of the Danube-Pontiac region represent an original group of soils within a single chernozem type of soil formation. Genetically, they are heterogeneous, but the parent rocks on which these soils form are always in a certain, usually significant, extent initially enriched in carbonates. All carbonate chernozems are characterized by a number of common features, mainly negative in agronomic terms: alkaline reaction from the surface, excess of carbonates, increased calcareous potential, low mobility of some microelements (Кирилюк, 2006).

Carbonate chernozems are lighter than other representatives types of the same granulometric composition are highly exposed to water erosion.

Carbonates content are the main diagnostic feature of this chernozem type. The arable layer of soil contains 1.2-6.9% of carbonates ($CaCO_3$). The content of $CaCO_3$ increases sharply at a depth of 60-100 cm. At the depth of 70-80 cm, soils contain more than 10% of carbonates. In the transition from one to the other degree of erosion, an increase in the $CaCO_3$ content occurs, from 1.2% in chernozem carbonate non-eroded (0-10 cm layer) to 7.0% in heavily eroded chernozem (*figure 1*).

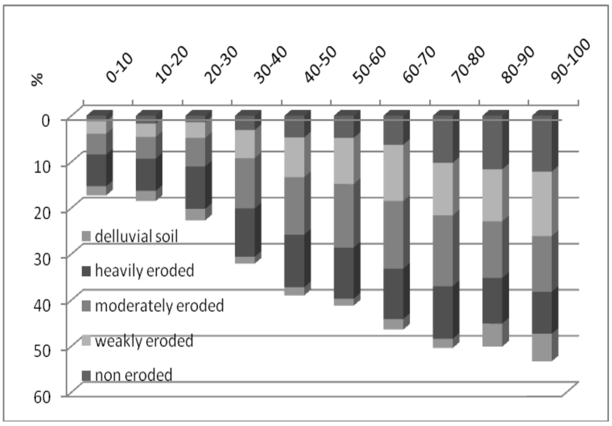

Figure 1 **Carbonates content in eroded soils**

Physico-chemical properties. A somewhat lower content of humus in carbonate chernozems is a consequence of the presence of $CaCO_3$ from the surface. Nevertheless, their humus profile is not specific, is typically black earth and reflects the features of the modern bioclimatic environment.

Information on the qualitative composition of humus in the carbonate chernozems is not numerous (Leah, 2010). The humus content with depth decreases very smoothly: in the arable layer of non-eroded carbonate chernozem its content is 3.84%, at a depth of 40-50 cm - 2.45%, at a meter depth - 0.90%. Consequently, the soil belongs to the powerful category. The amount of humus in the plow horizon of soils decreases, respectively, to the degree of erosion: 3.2% -2.7% -1.8% (*table 1*).

Table 1

Physico-chemical properties of eroded carbonate chernozem and diluvial soil

Horizon	Depth, cm	Humus %	*OD-ha	pH_{H2O}	$CaCO_3$, %	Ca^{2+}	Mg^{2+}	$\sum Ca^{2+} + Mg^{2+}$	$\frac{Ca^{2+}}{Mg^{2+}}$
						mg-equ./100 g of soil			
Chernozem carbonate - non eroded									
Ap.	0-10	3.84	47	7.8	1.18	22.8	3.2	26.0	7.1
	10-20	3.19	41	7.8	1.67	19.3	3.0	22.3	6.4
Chernozem carbonate - weakly eroded									
Ap	0-10	3.17	22	7.8	2.73	37.2	2.6	39.8	14.3
	10-20	3.10	15	7.8	2.90	27.9	2.1	30.0	13.3
Chernozem carbonate - moderately eroded									
ABp	0-10	2.70	18	7.9	4.53	45.6	2.3	47.9	19.8
	10-20	2.65	15	7.9	4.73	50.7	2.7	53.4	18.8
Chernozem carbonate - heavily eroded									
Bp	0-10	1.85	3	7.9	6.93	69.1	3.5	72.6	19.7
	10-20	1.75	1	7.9	7.00	77.9	3.6	81.5	21.6
Diluvial carbonate soil									
Ih	0-12	3.41	49	7.0	2.00	24.0	1.8	25.8	13.3
IIh	12-25	3.34	42	6.9	2.20	21.2	1.5	22.7	14.1

**OD-ha - optical density of humic acids*

With the increase of erosion degree, the content of exchangeable bases rise. Exchange Ca in non-eroded chernozem is 22.8 mg-equ./100 g of soil, and 69.1 mg-equ./100 g - in strongly eroded soil. The ratio of Ca and Mg in soils increasing, from 7 to 20, which indicates the availability of these elements for plants. The water pH varies insignificantly - 7.8-7.9.

Trace elements. Chernozems of Moldova has long represented the most important object for comprehensive research; they are attracting special attention at present due to soil degradation and anthropogenic pressure.

Copper. The average content of Cu in the chernozems of Moldova is 34.6 mg/kg (Лях, 1991). In the upper soil horizons of catena, the total content of Cu was: 22.7 - 20.8 - 18.1 - 14.7 - 15.5 mg/kg in dependence of erosion degree. Weakly-eroded carbonate chernozem loses as a result of erosion - 8.4% of total Cu, moderately eroded - 20.7%; heavily eroded - 35.2% in comparison with non-eroded soil. The mobile forms of Cu were up to 10% and range from 1.65 to 1.0 mg/kg, from non eroded to heavily eroded soil. Unavailable forms of Cu were 90%. The chemical forms associated with carbonates were 17-20% in the 0-20 cm soil layer. About 0.4% of Cu was associated with organic matter. Copper compounds in the composition of primary minerals increase with depth (*table 2*).

Table 2

Content and chemical forms of Cu in carbonatic chernozems, mg/kg, 0-20 cm

Carbonate chernozem	Cu total	mobile forms	Chemical forms of Cu compounds with				
			carbo-nates	organic matter	Fe-Mn oxides	minerals	
						clay	primary
Non eroded	22.7	1.75	3.8	0.42	10.6	2.7	5.7
Weakly eroded	20.8	1.54	3.7	0.25	10.2	2.5	4.8
Moderately eroded	18.1	1.32	3.3	0.23	9.2	2.4	4.0
Heavily eroded	14.7	1.00	3.0	0.21	8.3	3.2	5.5
Diluvial soil	15.0	1.00	4.0	1.00	6.5	2.0	2.4

Zinc. The average content of Zn in soils of Moldova consist 48.0 mg/kg (Лях, 1991). Carbonate chernozems are characterized by a high content of Zn total - up to 76.4 mg/kg of soil. With increasing of erosion degree, its content decreases and amounts in the 0-20 cm layer of weakly eroded chernozem was 63.2 mg/kg, moderately - 60.6, heavily - 52.7 mg/kg (*table 3*). With profile depth, Zn decrease occurs, in the carbonate horizons of all soils is in the range of 42-48 mg/kg from the global content. The chemical forms associated with Fe and Mn oxides reach 89-76% of the total content in the plow layer. With profile depth in all eroded soils, the compounds of Zn with oxides increase.

Nickel. The total content of Ni in study soils increases, from 48.9 mg/kg in non-eroded to 83.5 mg/kg - in heavily eroded carbonate chernozem. With depth, its content decreases in the underlying horizons of soils. Compounds Ni in composition of oxides of Fe and Mn make up the largest part: from 43 mg/kg (88%) in non-eroded to 29 mg/kg (35%) in heavily eroded chernozem (*table 4*). Acid-soluble, exchangeable and organic compound of Ni decrease with increasing of erosion degree (Лях, 2003, 2005a). The second place in the adsorption of Ni after oxides occupies the primary minerals. These compounds increase with profile depth in all soils of the catena with eroded varieties.

Table 3

Content and chemical forms of Zn in carbonatic chernozems, mg/kg, 0-20 cm

Carbonate chernozem	Zn total	mobile forms	Chemical forms of Zn compounds with				
			carbo-nates	organic matter	Fe-Mn oxides	minerals	
						clay	primary
Non eroded	76.4	2.45	3.2	0.60	40.0	23.4	12.4
Weakly eroded	63.2	1.34	3.0	0.55	45.0	21.0	23.6
Moderately eroded	60.6	1.32	2.4	0.50	50.0	16.6	29.7
Heavily eroded	52.7	1.30	1.7	0.45	56.0	10.5	51.2
Diluvial soil	41.4	3.85	5.5	0.10	22.0	20.0	13.5

Table 4

Content and chemical forms of Ni in carbonatic chernozems, mg/kg, 0-20 cm

Carbonate chernozem	Ni total	mobile forms	***Chemical forms of Ni compounds with***				
			carbo-nates	organic matter	Fe-Mn oxides	minerals	
						clay	primary
Non eroded	48.9	3.30	3.3	0.53	43.0	1.7	10.9
Weakly eroded	51.9	3.10	3.0	0.50	36.0	8.4	18.9
Moderately eroded	77.6	3.00	2.5	0.45	35.5	35.1	48.6
Heavily eroded	83.5	3.00	2.5	0.42	29.0	48.5	55.0
Diluvial soil	41.0	5.00	11.1	0.22	21.3	8.7	11.1

Cobalt. The average Co content in soils of Moldova is 15.0 mg/kg (Leah, 2005b). Carbonate chernozems non eroded are characterized by a high content of Co - up to 21.0 mg/kg. With an increase of erosion degree, its content decreases and consist 19.5-17.3 mg/kg in the 0-20 cm soil layer.

Oxides of Fe and Mn bind the largest part of the Co: from non eroded soil to highly eroded, they reach 62-75% of the total content in the arable horizon 0-20 cm. With increases of profile depth of the eroded soils, these compounds increase several. In the upper horizon of non-eroded chernozem, Co compounds with clay minerals account 14.3% of the total content.

Primary minerals retain almost the same content of Co as clay minerals. The accessible and mobile forms of Co in the 0-20 cm layer of soils consist 0.18-0.35 mg/kg (*table 5*).

Solubility and availability of Co in eroded carbonate chernozems increase in the horizons of calcium-saturated (horizon C) - 2.26-4.36%.

Between the concentration of mobile forms of microelements in soils and their content in plants there is a close relationship (r=0.65-0.95).

Under the influence of erosion, heavy metal compounds undergo a partial or complete change, and takes place their transformation. The study of the compounds transformation in soils provides additional information on the nature of the compounds formed in the soil.

Table 5

Content and chemical forms of Co in carbonatic chernozems, mg/kg, 0-20 cm

Carbonate chernozem	Co total	mobile forms	Chemical forms of Co compounds with				
			carbo-nates	organic matter	Fe-Mn oxides	minerals	
						clay	primary
Non eroded	21.0	0.18	2.4	0.10	13.0	3.0	2.5
Weakly eroded	19.5	0.25	2.3	0.10	14.0	2.0	2.3
Moderately eroded	18.0	0.30	2.1	0.10	15.0	1.5	1.8
Heavily eroded	17.3	0.35	2.0	0.10	17.0	1.0	1.2
Diluvial soil	19.7	0.40	3.3	0.10	19.0	9.0	1.7

CONCLUSIONS

- In the distribution of microelements in soils in terms of erosion, their mobility changes, which can serve as a diagnostic criterion for determining the type of pollution (anthropogenic or natural).
- Accumulation of microelements in plants on eroded carbonate chernozems can decrease as a result of antagonism of elements and the functioning of biochemical barriers.
- Carbonates in the soil contribute to fixing trace elements by reducing the content of their exchange forms and increasing the sorption capacity of Fe-Mn oxides.
- The studied features of the transformation of trace element compounds in eroded carbonate chernozems can be used to estimate the environmental impact of erosion and anthropogenic factors on the soils productive capacity.
- The established mechanisms of interaction of microelements with soil components can serve to develop effective methods of restoring soil fertility.
- The revealed patterns of translocation of microelements to plants can be applied for the purpose of normalizing their content in the soils of Moldova.
- Erosion is a factor that increases the carbonate content of chernozems in the plow horizon, which in turn weakens the anti-resistance of soils to anthropogenic influences.

REFERENCES

Leah T., 2005a – *Distribuţia nichelului în catena cu cernoziomuri carbonatice*. Ecological Chemistry. Chişinău, 484-489.

Leah T., 2005b – *Formele chimice ale cobaltului în cernoziomurile carbonatice erodate din Republica Moldova.* Soil resource use, environment protection and rural development in the western part of Romania. Vol.II. Bucharest, 11-19.

Leah T., 2010 – *Humus and trace elements as an indicator of eroded material from carbonatic chernozems.* Agriculture and Environment. Scientific paper. Series A. Vol. LIII. Agronomy. Buharest, 22 -28.

Атлас Почв Молдавии, 1988 - *Отв. ред. И.А. Крупеников*, Кишинёв, Штиинца, 83-88.

Кабата - Пендиас А., Х. Пендиас, **1989** - *Микроэлементы в почвах и растениях*. Москва, Мир, 1989.

Кирилюк В. П., 2006 - *Микроэлементы в компонентах биосферы Молдовы.* Chişinău, Pontos, 156 с.

Крупеников И. А., 1979 - *Карбонатные черноземы*. Кишинев, Штиинца, 108 с.

Лях Т. Г., 1991 - *Соединения меди и цинка в эродированном карбонатном черноземе.* Сб.: Антропогенная эволюция, оценка и методы изучения почв и почвенного покрова. Кишинев, с. 107-118.

Лях Т. Г., 2003 - *Формы соединений кобальта и никеля в эродированных карбонатных черноземах Молдовы*. Сб. докладов Международной научно-практической конференции «Модели и технологии оптимизации земледелия», Курск, с.152-155.

Содержание и формы микроэлементов в почвах - 1979. Под ред. Н. Г. Зырина. Изд. МГУ, 285 с.